

Self-Assembled and Langmuir-Blodgett Arachidic Acid Monolayers on Silver: A Comparative Reflection-Absorption Fourier Transform Infrared Spectroscopic Study

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Self-assembled (SA) and Langmuir-Blodgett (LB) monolayers of arachidic acid on silver surfaces have been investigated by a reflection-absorption Fourier transform infrared spectroscopy. Arachidic acid was adsorbed on silver as carboxylate with its two oxygen atoms bound symmetrically to the surface. Although both the SA and LB monolayers consisted of fully extended trans zigzag carbon chains, a closer examination indicated that the SA monolayers should possess a more ordered crystalline structure than the LB monolayers. The infrared spectral data dictated that the extent of methyl group exposure at the air-film interface was greater in the SA monolayers than the LB monolayers, in agreement with the contact angle measurement. From a theoretical analysis, the alkyl chains in each monolayers seemed to be tilted away from the surface normal by less than 3.5° , but in opposite directions. Arachidic acid monolayers were concluded to have same structure as stearic acid monolayers.

Introduction

Ordered monolayers of long chain organic amphiphiles are of great interest for their fundamental importance in understanding interfacial properties as well as their application in the areas of boundary lubrication, corrosion inhibition, adhesion and catalysis.¹⁻⁴ Such organized monolayers have been usually established either by Langmuir-Blodgett (LB) deposition technique^{4,5} or by spontaneous adsorption from solution, known as self-assembly (SA)^{4,6} method.

It has been generally recognized that the monolayers prepared by the SA method are very similar to those prepared by the LB technique.⁴ However, the direct comparative study on their structural details has been scarcely reported.⁷ Saturated fatty acids adsorbed on aluminum by the SA method were claimed by Gun *et al.*⁸ to have similar structure to those prepared by the LB method. Recently, we have found that stearic acid monolayers anchored to silver by the SA method possessed a more ordered crystalline structure than those prepared by the LB method.⁹ A natural question arises whether the observation made for stearic acid is applicable equally to other fatty acids. In this respect, we have performed the infrared reflection-absorption (IRA) spectroscopic investigation to clarify the structural similarity and/or difference between the LB and SA monolayers of arachidic acid, another prototypical fatty acid with even number of carbon atoms, adsorbed on the silver surface.

Experimental

The substrates were prepared by evaporating silver at 10^{-5} – 10^{-6} torr (1 torr = 1.33×10^2 Pa) on batches of previously sonicated 2.5×3.7 cm glass slides. After a near 200 nm deposition, the evaporator was backfilled with nitrogen to reduce the ambient contamination. The substrates prepared in the same batch were used equally for the deposition of LB and SA monolayers.

To prepare the LB monolayer, a computerized home-made LB trough was employed. Initially, 10^{-2} M arachidic acid

($C_{19}H_{39}COOH$) in chloroform was spread onto the water sub-phase. After evaporation of the solvent, the monolayer was compressed at a constant rate of $2.0 \text{ cm}^2/\text{min}$ up to the surface pressure of 30 mN m^{-1} . The π -A isotherm at 20°C showed that the monolayer was a solid condensed film at this pressure. Maintaining the surface pressure at 30 mN m^{-1} , the condensed film was transferred to the silver surface by raising the immersed substrate at a rate of $1.0 \text{ mm}/\text{min}$. The present transfer rate was found slow enough for the preparation of LB monolayers with an optimal ordering.

The SA monolayer was prepared by dipping the silver substrate into 10^{-3} M arachidic acid in ethanol. The solution was initially bubbled with nitrogen, and the whole SA system was kept in the N_2 -purged dry box during the film deposition.

The infrared spectra were obtained with a Bruker IFS 113v Fourier transform spectrometer equipped with a mercury cadmium telluride detector. To record the IRA spectra of arachidic acid adsorbed on the silver substrate, a specular reflection attachment (Harrick VRA) was used in conjunction with a Harrick wire grid polarizer. The angle of incidence for the p-polarized light was set at 80° . Each spectrum was obtained by averaging 2048 interferograms at 4 cm^{-1} resolution. To reduce the effect of water vapor rotational lines on the absorption spectra, the sample and reference interferograms were devised to be recorded alternately after every 32 scans. The Happ-Genzel apodization function was used in Fourier transforming the interferograms. All IRA spectra are reported as the $-\log(R/R_0)$, where R and R_0 are the reflectivities of the sample and the bare clean silver substrate, respectively.

Besides the IR spectra, contact angle measurements were also undertaken for the LB and SA monolayers by using a home-made goniometer. The static contact angles determined with water drops were observed to be reproducible to within 3° for every sample.

Unless otherwise specified, all chemicals and gases were reagent grade and used as received. The triply distilled water, whose resistivity was greater than $17.5 \text{ M}\Omega$, was used throughout in the preparation of LB monolayers.

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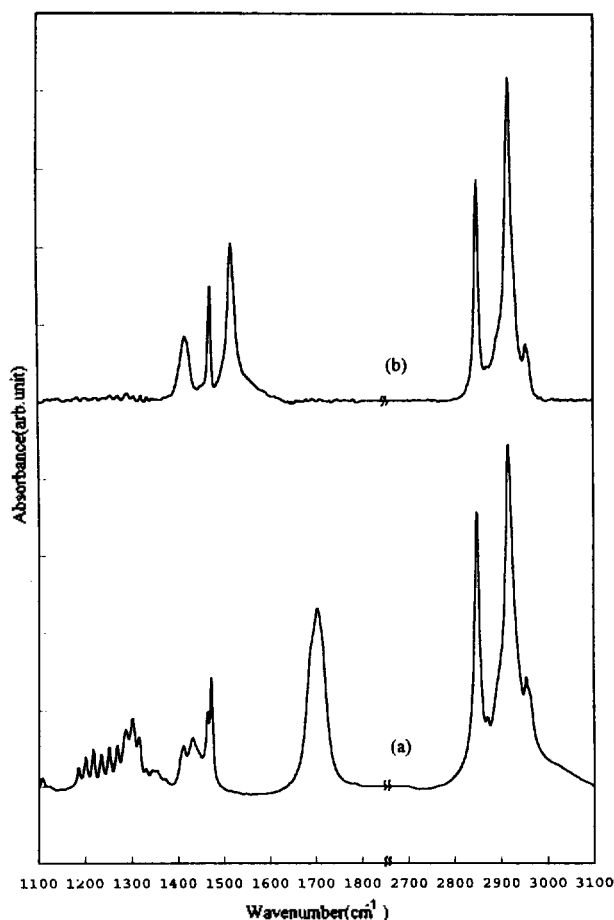


Figure 1. Infrared transmission spectra of arachidic acid (a) and its silver salt (b) dispersed in KBr matrix. Silver arachidate was prepared by reacting arachidic acid with silver nitrate in ethanol.

Results and Discussion

It would be worth to mention that since the surfaces used for both the SA and LB monolayers were prepared in identi-

cal condition, any spectroscopic differences observed between the two monolayers could be considered as due to the method of monolayer formation, independent of surface roughness effects.

In order to help interpret the IRA spectra, the transmission IR spectra of arachidic acid and its silver salt were recorded initially in KBr matrices. The corresponding spectra are shown in Figure 1(a) and 1(b), respectively. The peak positions and their appropriate vibrational assignments are collectively summarized in Table 1. The spectral pattern of the acid spectrum in the 3000-2800 cm^{-1} region is very close to that of the salt spectrum. However, a significant spectral difference is observed in the 1800-1400 cm^{-1} region. The ν (C=O) band¹⁰ appears distinctly at 1703 cm^{-1} in the acid spectrum but absent in the salt spectrum. Instead, the ν_s (COO⁻) and ν_{as} (COO⁻) bands¹¹ are observable in the latter spectrum at 1417 and 1518 cm^{-1} , respectively. This implies that silver atoms are symmetrically bonded to the carboxylate group. The so-called progressional bands appearing in the 1200-1350 cm^{-1} region in Figure 1(a) is known to indicate that the alkyl chains are fully extended in the solid state with a trans zigzag structure.¹² We can identify the presence of progressional bands also in the salt spectrum albeit their peak intensities are much weaker than those in the acid spectrum.

As for the case of stearic acid,⁹ arachidic acid was adsorbed on the silver surface very favorably. The IRA spectra and the contact angles of arachidic acid self-assembled on the silver substrate were observed to be nearly independent of the immersion time. The films obtained within 1 hour immersion were hardly different from those obtained after 8 day immersion. These observations suggest that the adsorption of arachidic acid on the silver surface is energetically very favorable and thus a complete monolayers can be formed readily by contacting the silver substrate with the acid solution.

The IRA spectra of LB and SA monolayers on the silver surfaces in the 1800-1100 cm^{-1} region are shown in Figure 2(a) and 2(b), respectively. The latter spectrum corresponds

Table 1. Vibrational Mode Assignments of Arachidic Acid (ARCA)^a

$\text{C}_{19}\text{H}_{39}\text{CO}_2\text{H}$	$\text{C}_{19}\text{H}_{39}\text{CO}_2\text{Ag}$	SA ARCA/Ag	LB ARCA/Ag	Assignment ^{b,c}
		2964	2964	CH ₃ asym str
2954	2954			CH ₃ asym str
		2937	2937	CH ₃ sym str ^d
2917	2917	2916	2916	CH ₂ asym str
2871	2871	2877	2877	CH ₃ sym str
2849	2849	2850	2850	CH ₂ sym str
1703				C=O str.
	1518			COO ⁻ asym str
1471	1471	1471	1471	CH ₂ scissors def.
1464		1464	1464	
1431				C-O str+OH def
	1417	1407	1403	COO ⁻ sym str
		1382	1384	CH ₃ sym def
	1150-1350	1150-1350	1150-1350	CH ₂ wagging+twisting

^aWavenumbers in cm^{-1} . ^bAssigned based on refs. 10, 11, and 27-30. ^cstr: stretching, def: deformation. ^dIn Fermi resonance with overtone of CH₃ asym def., and crystalline transition.

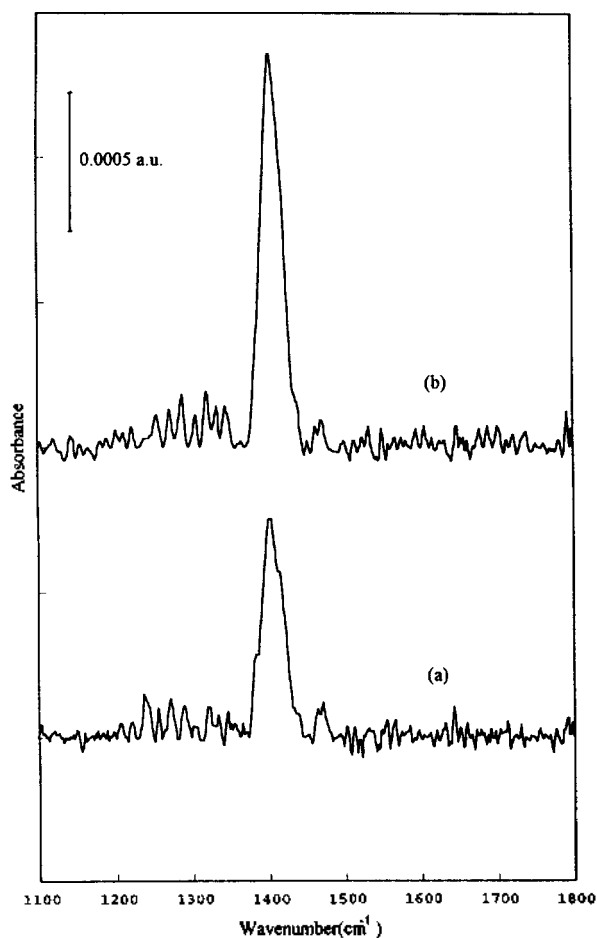


Figure 2. Infrared reflection-absorption spectra of arachidic acid monolayers adsorbed on silver by Langmuir-Blodgett (a) and self-assembling (b) methods in 1800-1100 cm^{-1} spectral region.

to what was obtained after 1 hour immersion, but practically the same as those obtained after further immersion. It is seen that the spectral pattern of LB monolayers is very close to that of SA monolayers. In both spectra, the C=O stretching band which appeared at 1703 cm^{-1} in Figure 1(a) was completely absent. This absence, together with the presence of the symmetric stretching bands of COO^- group at 1403 cm^{-1} for the LB monolayers and at 1407 cm^{-1} for the SA monolayers, dictates that the adsorption process results in the formation of carboxylate salts. The fact that the asymmetric stretching band [$\nu_{as}(\text{COO}^-)$] is hardly detectible in the IRA spectra suggests further that the two oxygen atoms of carboxylate group lie parallel to the silver substrate. That is, the carboxylate head group should be bound at the silver substrate symmetrically. This conclusion is based on the well-known infrared surface selection rule¹³⁻¹⁶ that vibrational modes whose dipole moment derivatives possess components normal to the metal surfaces are preferentially excited. The present observation made on arachidic acid is much the same as that on stearic acid reported earlier. As in the case of stearic acid, it is not evident, however, whether the carboxylate group binds to the silver surface as a bridging or a bidentate form. Referring to the X-ray crystallographic data on the various silver salts,^{17,18} the bridging form was claimed in our previous work⁹ to be more probably to occur.

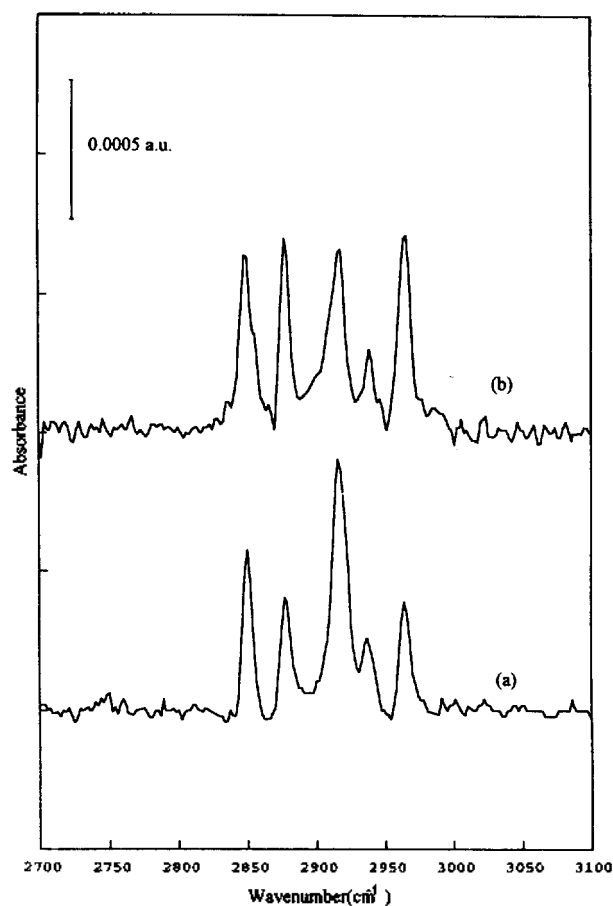


Figure 3. Infrared reflection-absorption spectra of arachidic acid monolayers adsorbed on silver by Langmuir-Blodgett (a) and self-assembling (b) methods in 3100-2700 cm^{-1} spectral region.

Even in that case, each oxygen atom in the monolayers was argued to be affected greatly by the silver atoms residing near at the directly coordinated silver atom since the frequency of the $\nu_s(\text{COO}^-)$ mode in the surface spectra (Figure 2) was 10-14 cm^{-1} different from that in the salt spectrum (Figure 1(b)).

The progressional bands occur from coupling between twisting and wagging of CH_2 units trans to each other and are enhanced greatly by a polar head group bonded to the methylene unit.^{11,12} The appearance of progressional bands in the 1200-1350 cm^{-1} region in the surface spectra is then indicative of existence of fully extended trans zigzag molecular chains in both the LB and SA monolayers. This implies that the development of twisting or strain in the methylene units is rather infeasible during the monolayer formation. The present observation is consistent with the general view that the LB monolayers are composed of well-ordered close packed structure. The present work dictates further that the SA monolayers of arachidic acid should also consist of fully extended close packed structure as likely the case of stearic acid.⁹

It is seen that the $\nu_s(\text{COO}^-)$ band in the surface spectra is several times broader than that in the salt spectrum. Considering that the monolayers are composed of fully extended trans zigzag chains, this can be ascribed to the opening of new vibrational relaxation channel (from adsorbate to subst-

rate) rather than to the existence of various twisted or strained alkyl chains. Since the methyl group is connected to the carboxylate *via* the saturated methylene units, the methyl group vibrational modes will be barely affected by the newly opened relaxation channel. Then, comparing the relative bandwidth of $\nu_{as}(\text{CH}_3)$ and $\nu_s(\text{COO}^-)$ modes in the salt spectrum with that in the surface spectra (Figure 2 and 3), the $\nu_s(\text{COO}^-)$ band could be estimated to have broadened by *ca.* 3 times *via* the adsorbate to metal vibrational relaxation channel.

While it has been suggested that both the LB and SA monolayers are aligned in a well-ordered close-packed structure, closer examination of the band shapes and intensities indicates that the structure of LB monolayers should be somewhat different from that of SA monolayers. It is seen from the surface spectra that the integrated intensity of $\nu_s(\text{COO}^-)$ band is more or less greater in the SA spectrum than that in the LB spectrum. Assuming that the packing density of LB monolayers is same as that of SA monolayers, the present observation indicates that the $\text{C}_1\text{-C}_2$ axis of arachidate in the SA monolayers should have a more perpendicular stance with respect to the metal surface compared with that in the LB monolayers. This seems consistent with what was observed for the CH_3 deformation mode, i.e., the mode which appears as a shoulder peak at near 1384 cm^{-1} is more distinct in the LB spectrum rather than in the SA spectrum. The argument that the SA monolayers possess a more perpendicular orientation than the LB layers can be further confirmed from both the surface spectral pattern in the C-H stretching region and the contact angle measurement as to be discussed below.

The IRA spectra of LB and SA monolayers on the silver surfaces in the C-H stretching region are shown in Figure 3(a) and 3(b), respectively. In both spectra, the peak known to arise from a Fermi resonance interaction between the symmetric stretching vibration and the overtone of asymmetric deformation of the methyl group in a crystalline state appeared clearly at 2937 cm^{-1} . This suggests that the LB and SA layers are all present in crystalline states.¹⁹ In conjunction with the progression bands, the monolayers can be concluded to be composed of fully extended trans zigzag molecular chains assembled in a crystalline state.

The relative peak intensities in the IRA spectra are significantly different from those in the salt spectrum. This indicates that the monolayers are very anisotropic. Although the peak positions are close to each other, the spectral pattern for LB monolayers is, however, somewhat dissimilar to that for SA monolayers. Comparing with the salt spectrum, the symmetric stretching band of CH_3 group centered at 2877 cm^{-1} is observed to be much intense in the surface spectra. In addition, the $\nu_s(\text{CH}_3)$ band is found as strong as the $\nu_{as}(\text{CH}_3)$ band in the SA spectrum. According to the surface selection rule, this dictates that the $\text{H}_3\text{C-CH}_2$ bond in the SA monolayers should possess a more perpendicular stance with respect to the silver surface than that in the LB monolayers. Considering that arachidic acid contains even number of carbon atoms, the present observation implies that the molecular chain in the SA monolayers must be more perpendicular to the surface compared with that in the LB monolayers (*vide infra*). This suggests that the degree of exposure of CH_3 group in the air-monolayer interface is larger in the

Table 2. Direction of transition dipole moments for C-H stretching vibrations

Assignment	Frequency (cm ⁻¹)	Direction of transition dipole moment
CH_3 asym(ip) ^a	2964	in plane to CCC backbone plane and normal to the C-CH ₃ bond
CH_3 asym(op) ^a	2954	normal to the CCC backbone plane
CH_3 sym	2871	parallel to the C-CH ₃ bond
CH_2 asym	2917	normal to the CCC backbone plane
CH_2 sym	2849	in plane to CCC backbone plane and in plane to HCH plane

^aip denotes in-plane mode and op denotes out-of-plane mode.

SA layer than in the LB layer. This view is consistent with the contact angle measurement that the static contact angles of water are 102° and 107° for the LB and SA monolayers, respectively.

IRA spectra can be simulated with the information on the complex refractive indices of adsorbed layer and metal substrate and the transition dipole moments of the absorption bands. In this sense, a more quantitative comparison was attempted to be made regarding to the molecular orientation of SA and LB monolayers. The IRA spectral pattern in the C-H stretching region was accordingly simulated by using the Hansen's model.²⁰ Initially, the absorbance of silver arachidate diluted in KBr matrix was measured. From this, the imaginary part, h , of the complex refractive index for silver arachidate was obtained *via* the relation²¹ $h=A/4\pi vdc$, in which A is the apparent absorbance, v is wavenumber, and d and c are, respectively, the optical thickness and concentration of infrared absorber. The Kramers-Kronig relation²² was then applied to evaluate the real part of the complex refractive index. The refractive index of silver metal was taken from the work of Ordal *et al.*²³ The directions of the transition dipole moments in the CH_2 and CH_3 stretching vibrations are well established for aliphatic alkane chains by Snyder *et al.*,^{24,25} and they are reproduced in Table 2. Based on these informations, theoretical IRA spectra were obtained as a function of tilt and twist angles, defined, respectively, as the angle between the direction of CCC backbone and the surface normal and the angle between the CCC backbone plane and the surface normal plane (see Figure 4). The simulated IRA spectrum best fit to the experimental one was found when the tilt and twist angles were set, respectively, at 2.5° and 2.0° for the SA monolayers and at -3.5° and 3.5° for the LB monolayers. It has to be mentioned that substantial spectral mismatch occurs when either the tilt or twist angle is changed even by 1° from the values reported here.

The above calculation suggests that the alkyl chains are nearly perpendicular to the surface in both the SA and LB monolayers. This seems consonant with the earlier report²⁶ that the hydrocarbon backbone of the cadmium arachidate LB assemblies is tilted away from the surface normal by less than 5° . Nonetheless, the present work reveals that the direction of tilt, albeit small, is different between the SA and LB monolayers of arachidic acid. The fact that the tilt angle for the SA monolayers is positive while that for the

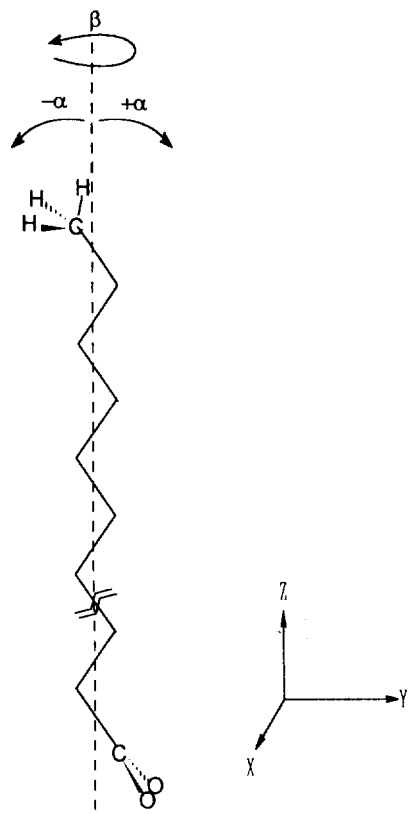


Figure 4. Representation of the model used in calculation of the stretching band intensities of CH_3 and CH_2 groups as functions of chain orientation relative to the substrate surface. α and β correspond, respectively, to the angle of chain tilt and the angle of chain twist.

LB monolayers is negative implies that the extent of exposure of the methyl group in the air-monolayer interface should be larger in the former than in the latter as invoked previously. In these orientations, the symmetric stretching band of carboxylate group is also expected to be stronger in the IRA spectrum of SA monolayers compared with that of LB monolayers as actually observed.

The C-H stretching peaks in the LB monolayers are broader than those in the SA monolayers. For instance, the ν_{as} (CH_2) peak at 2916 cm^{-1} and the Fermi resonance interaction peak at 2937 cm^{-1} are well resolved in the SA spectrum but are substantially merged into each other in the LB spectrum. This suggests that the LB assemblies are less ordered than the SA assemblies. Although the average tilt angle is about -3.5° , the strong intensity of CH_2 asymmetric stretching bands in the LB spectrum may imply the distribution of trans zigzag molecular chains in variable angles. Some twisted chains around certain methylene units may also contribute to the higher intensity. That is, during the liquid-to-solid state transition in the Langmuir trough some twisted chains could exist on the water subphase, and such twisted chains, albeit in part, might still remain even after the LB transfer. Hence, although the LB monolayers are invoked generally to be composed of well-ordered close-packed structure, their orderness appears not so much optimal as that of SA monolayers.

The initial driving force to form the SA monolayers is the chemical interaction between the head group and the metal surface. The formation of strong bond between the adsorbate and the substrate is a prerequisite to a successful chemisorption. The van der Waals type interaction between the molecular chains becomes then important allowing the surface anchored adsorbates to aggregate into a well-ordered two dimensional structure. In the LB process, the initial driving force is generally dipolar type interaction between the adsorbate and the substrate. In this case, the van der Waals interaction between the chains is as equally important as the head group-to-substrate interaction. Then, during the LB deposition of arachidic acid onto the silver substrate, the deprotonation of carboxylic group and its subsequent chemical interaction with the metal surface may not be effectively to occur. When such a COO^- -Ag bond is not formed very efficiently during the LB process, some water molecules produced by the deprotonation may also be incorporated at near the metal surface. Furthermore, once the Langmuir layer in the water subphase is transferred to the substrate as a LB layer, the reorganization of monolayers will be hardly to take place in the ambient condition. Based on these arguments, we could rationalize the observation made here that the SA monolayers possessed a more ordered structure than the LB monolayers. When the formation of chemical bond between the adsorbate and the substrate is very favorably to occur, well organized monolayers seems to be assembled on the solid substrate by the self adsorption process in the solution phase.

Finally, it would be worth to mention that the monolayers of arachidic acid formed on the silver surface are structurally very rigid. As a separate experiment, it has been examined whether the LB monolayers once formed on the silver substrate could experience a structural change as the LB film was immersed in the solution used in the self-assembly. Even after an one-day immersion, the IRA spectrum was observed hardly to change. This indicates that both the SA and LB monolayers are very stable and consist of very rigid two dimensional structures. This is also consistent with what was observed for stearic acid.

In summary, a comparative infrared spectroscopic study of self-assembled and Langmuir-Blodgett monolayers of arachidic acid on silver surfaces has been performed. The adsorption of arachidic acid on the silver surface occurred very favorably in the liquid state after deprotonation. The carboxylate head group was found to be anchored to silver symmetrically. The monolayers prepared by either SA or LB methods appeared to possess a close-packed crystalline structure with fully extended trans zigzag carbon chains. A closer examination indicated that the SA monolayers were, however, more ordered than the LB monolayers. Moreover, the molecular chains of SA monolayers seemed to assume a slightly more perpendicular stance with respect to the surface. This led to the conclusion that the extent of methyl group exposure at the air-film interface is greater in the SA monolayers than the LB monolayers. This could be confirmed further from the contact angle measurements. As a closing remark, the structure of arachidic acid monolayers was found to be almost the same as that of stearic acid monolayers.

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Syntheses and Properties of New Nickel(II) Complexes of 14-Membered Pentaaza Macrocyclic Ligands with C-Nitro and N-Alkyl Pendant Arms

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Square planar nickel(II) complexes with various 1-alkyl derivatives of the 14-membered pentaaza macrocycle 8-methyl-8-nitro-1,3,6,10,13-pentaazacyclotetradecane can be readily prepared by two-step metal template condensation reactions of ethylenediamine, nitroethane, formaldehyde, and appropriate primary alkylamines. In coordinating solvents the nickel (II) complexes form octahedral species containing two axially coordinated solvent molecules and thus show square planar-octahedral equilibrium. The properties of the pentaaza macrocyclic complexes are considerably different from those of the complexes of analogous hexaaza and tetraaza macrocyclic complexes. Synthesis, characterization, and spectroscopic and chemical properties of the new complexes are described.

Introduction

Many works have been concerned with the synthesis of new types of polyaza macrocyclic ligands and complexes, since the properties of such compounds are closely correlated with their structural characteristics. Various saturated polyaza macrocyclic complexes have been prepared by one-pot reactions of complexed amines with formaldehyde.¹⁻¹⁰ For example, the nickel(II) complexes of the hexaaza macrocycles

1a-1d,^{5,6} which contain two alkylamino bridging groups in the six-membered chelate rings, have been synthesized by the reactions of Eq. (1). It has also been reported that the reaction Eq. (2) of ethylenediamine, formaldehyde, and nitroethane in the presence of nickel(II) ion produces the complex of the tetraaza macrocycle 2 containing the nitroethane bridging groups.⁸ The hexaaza and tetraaza macrocycles are known to behave as tetradentate ligands; the two tertiary nitrogen atoms or nitro groups of the ligands are not involv-